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A Comprehensive Study of Surface Chemistry for Application to Engine NO_x Aftertreatment

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Problem Definition:

This work focuses on developing a scientific understanding of the processes associated with NO_x trap operation. NO_x traps are the most advanced technology for achieving future emissions standards with diesel engines. Successful development of NO_x traps will allow widespread use of diesel engines in light-duty vehicles, reducing oil imports by as much as 60%.

Diesel engines have a high efficiency and low maintenance that makes them the ideal choice for transportation applications. Use of diesel engines in all light-duty vehicles would reduce oil consumption in the USA by 30% and oil imports by 60%, considerably improving our energy security. For heavy trucks, there is no viable alternative to diesel engines. Only diesel engines can provide the necessary high efficiency and long life. These benefits are offset by high emission of pollutants. Diesel engines have high emissions of NO_x and particulate matter. Over the last 20 years, EPA has been reducing allowable emissions from diesel engines, and NO_x emissions are scheduled to be cut by a factor of 10 over the next 7 years (see Figure 1). The target NO_x emissions for year 2010 is 0.20 g/hp-hr. This value is well below 1 g/hp-hr, which has been identified by one of the authors (Pitz [1]) as the minimum possible NO_x emission that can be obtained in a diesel engine with satisfactory combustion and without exhaust aftertreatment. An 80% efficient aftertreatment system is therefore necessary for achieving the 2010 NO_x emissions regulation. Achieving this level of diesel aftertreatment efficiency is a daunting task, and one that will require a strong research effort.

Purpose:

Manufacturing diesel aftertreatment systems with 80% efficiency for model year 2010 is an extremely difficult task. Our advanced analysis tools (computational chemistry linked with fluid mechanics and heat transfer) can be used to analyze and optimize NO_x traps, which are the system of choice for diesel engine aftertreatment.

NO_x adsorbing catalysts operate by adsorbing the NO_x in the exhaust stream during regular engine operation. After a period of time (1 minute), the catalyst saturates and has to be regenerated. Regeneration is achieved by injecting a reductant (typically fuel, although hydrogen or ammoniac can also be used) into the catalyst. The adsorbed NO_x desorbs under rich conditions, and then reacts with the reductant, producing molecular nitrogen, water and carbon dioxide. The regeneration cycle typically lasts about 2 seconds. After the regeneration cycle, the catalyst is ready for a new adsorption cycle.

Intermittent regeneration of the catalytic surface is a complex process, and much of the basic science behind this process is not understood. Unsolved scientific problems include the development of chemical kinetic mechanisms for surface chemistry; the analysis of sulfur

poisoning of the catalyst surfaces and the phenomenon of thermal aging of the catalyst materials. The adsorption and regeneration processes are dependent on gaseous flow rate, surface chemical kinetics and converter geometry. A comprehensive study of this process is of great importance to achieve the desired system efficiency for NO_x reduction. The possibilities and future market opportunities are enormous.

This project supports the DOE mission by improving national security through reduced dependence on foreign oil. This work also provides an opportunity for enhancing our surface chemistry analysis capabilities, which have great applicability to missile reentry, fuel cells, and sensors for chemical warfare agents and explosives detection. In addition to this, we will help the US industry remain competitive and will help clean up the environment.

Activities:

We have used Molecular Dynamics to characterize the basic physics of NO_x adsorption onto barium oxide catalysts. We also have used thermo-fluids models for NO_x traps to validate the molecular dynamics results and conduct detailed analysis and optimization of NO_x traps. Deep scientific understanding of NO_x trap processes will greatly assist manufacturers in meeting future emissions standards.

We have studied the microscopic mechanisms for trapping and release of NO_x species on the surface of a barium oxide (BaO) catalyst. To this end, we use the Car-Parrinello molecular dynamics (CPMD) method in conjunction with Vanderbilt pseudopotentials. Calculations were performed on bulk BaO to test the validity of our parameters.

The next step is to perform calculations of bulk BaO surface at finite temperature. We found that the dispersion in the bands of BaO is quite large, and therefore many layers of the surface must be included in order to achieve a stable surface. We found this number of layers to be at least six. With this many layers included in the calculation the calculations become prohibitive. Thus, we also chose to adapt the frozen lattice approximation in order to achieve some early results. To this end, we ran two sets of calculations at 300 K using CPMD. The first was a single NO_2 molecule adsorbed on a BaO surface. Our findings of this structure at 0 K are consistent with the findings of published data. The second calculation was two NO_2 molecules on a BaO surface (Figure 2). Our findings at 0 K are consistent with computational studies of NO_2 on MgO surfaces, namely the stable 0 K structure is a charge-separated species of NO_2^- and NO_2^+ . The charge transfer between the two NO_2 species allows them to be more strongly adsorbed to the BaO surface than neutral NO_2 species. Also note in Figure 2 the interesting orientation of the NO_2 species, one with the oxygen facing away from the BaO surface and the other with the oxygen facing toward the BaO surface. It is expected that if additional NO_2 's were added, the "one up, one down" orientation of the NO_2 would be repeated. This is consistent with published computational findings for NO_2 adsorption on MgO surfaces. However, no studies exist of the structures at 300 K. Our initial results indicate that as the temperature is raised from 0 K to 300 K on BaO , there is a charge transfer event back to the neutral NO_2 moieties. If this result holds, then the kinetics of trapping at 300-500 K is leading to a very different picture than calculations at 0 K.

We have also developed a 1-dimensional thermal and fluid mechanics model of a NO_x trap. The model currently uses generic chemical kinetic equations available from the literature. This

model will be used to validate the mechanisms obtained from our analysis by performing comparisons with the experimental results obtained at Caterpillar, PNNL and ORNL.

Technical Outcome :

The aim of this study is to understand in the microscopic mechanisms for trapping and release of NO species on the surface of barium oxide (BaO) catalyst. The challenge of this problem from a computational point of view is many-fold. For one, there is little data in the literature on the electronic structure of bulk BaO, so the choice of computational parameters (e.g. lattice constants, pseudopotentials, and cut-offs) is basically unknown. The other issue pertains to the choice of adsorbing species, NO₂. NO₂ is a radical which means that one of the orbitals has occupation unity. Computationally speaking this requires that each electron be treated as a separated degree of freedom which then doubles the computational effort to treating the BaO surface from the start. There have been recent computational studies of NO_x on BaO surfaces performed with density functional theory methods. In this investigation, the geometries of NO moieties on the BaO surface were studied at 0K. There are many approximations that were made in this study that we would like to improve upon. First, since the catalysts operate at between 300-500K, we would like to understand the NO_x moieties under these more realistic conditions. Second, the BaO lattice was not allowed to relax. Therefore, the precise nature of how the phonon modes couple to the NO_x will be unknown unless this restriction can be relaxed. As of mid-year we considered the use of Vanderbilt pseudopotentials in conjunction with Car-Parrinello molecular dynamics (CPMD) to investigate the structure of BaO. The goal of this was to reduce the computational costs. As of mid-year we reached our goal of simulating a fully loaded surface of BaO with NO₂ moiety at 500K, the operating temperature of a NO_x trap in a working engine (see attached movies). Our conclusion from this pioneering study is that geometries obtained by studying the system at 0K *may not* correspond to actual structures obtained at the working temperature in a diesel engine. There were two issues that still needed to be resolved. As of mid-year we wanted to stay with a more computationally tractable "frozen" lattice (keeping the BaO molecules fixed). In order to have confidence in our new results, we had to convince ourselves that the lattice does not play a significant role in the chemi/physi-sorption. The second issue was concerning the extent of a perfect BaO crystal representing an active NO_x trap.

We have addressed both of these issues. First, we are now using norm-conserving pseudopotentials with a cut-off of 100 Rydbergs and using the generalized gradient approximation for the exchange and correlation functional. This produced remarkable results for bulk and surface structure of BaO (see Fig. 1). Using the peta-scale resources at LLNL, we are able to perform calculations on a 2x2x2 unit cell, only fixing the bottom-most layer to the bulk value (as commonly performed) and allowing for full relaxation of the remaining degrees of freedom. The second issue pertains to the supporting medium. Recent experiments have isolated, through infra-red spectroscopy, the presence of BaCO₃ in the witherite structure. This is not so surprising since NO_x traps operate in a CO₂ rich environment. In order to see if the mechanisms of chemi/physi-sorption are similar to the BaO, we chose to perform calculations at finite temperature using witherite as the NO_x trap (see Fig. 2). The same pseudopotentials and exchange and correlation functionals were used as in the case of BaO.

Future work will focus on corroborating our findings at finite temperature and documenting the electron transfer with Wannier function analysis. Once this has been achieved, and we can

perform calculations to determine and compare the binding energies of a variety of NO_x moieties on fully relaxed surfaces of BaO and BaCO_3 .

Conclusions:

This project focuses on the scientifically and technically important problem of analyzing and modeling NO_x traps for diesel engine aftertreatment. We conducted an analysis based on a combination of analysis tools: a molecular analysis code for determining the basic reaction characteristics of the system and a fluid mechanics and heat transfer code to validate the results against experimental data. The work sheds new light on the processes that control the adsorption and desorption of NO_x molecules on barium substrates, and will be of great practical utility for designing improved NO_x traps.

References:

1. Flynn, P.F. ; Hunter, G.L. ; Farrell, L. ; Durrett, R.P. ; Akinyemi, O. ; Westbrook, C.K. ; Pitz, W.J. ; Loye, A.O. Zur , " The inevitable viability of engine -out NO_x emissions from spark -ignited and diesel engines, " Proceedings of the Combustion Institute, V.28, n1, 2000, p1211 -1217.

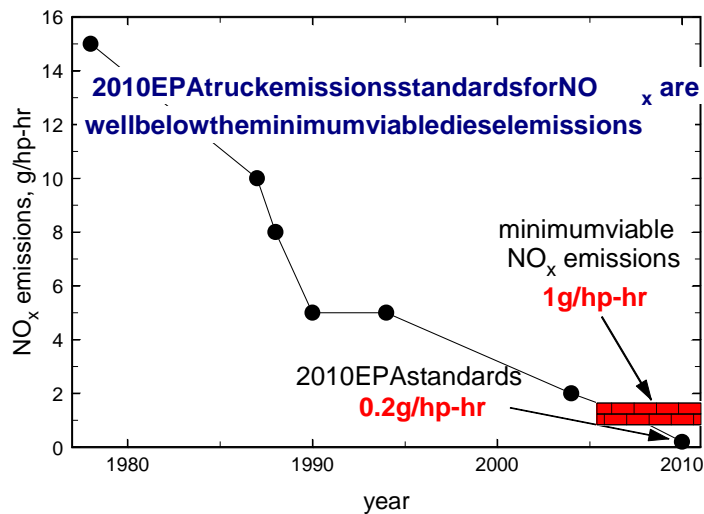


Figure 1. Evolution of NO_x and PM emissions standards for heavy-duty diesel engines. The figure also shows how the minimum NO_x emissions that can be obtained from a diesel engine with no aftertreatment.

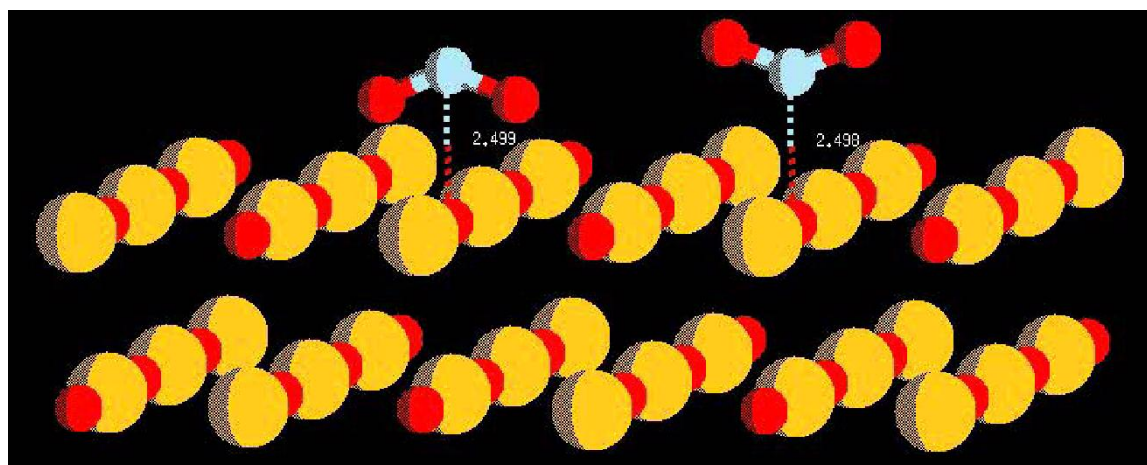


Figure 2. First-principles CP molecular dynamics simulation of NO_2 storage on a Barium-oxide surface using the MCR cluster.

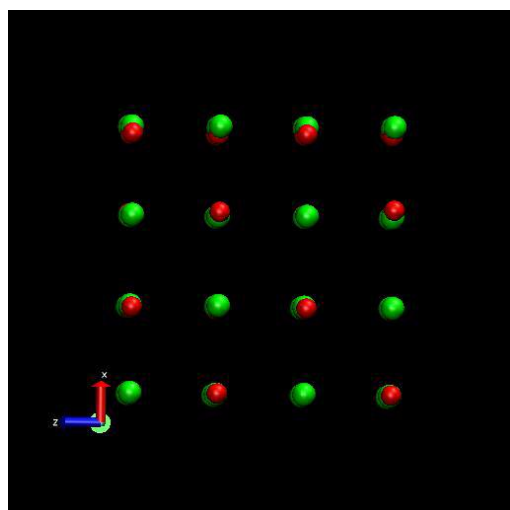


Figure 3. Relaxed surface of BaO. The bottom layer is fixed. One can discern a slight relaxation of the oxygens in the topmost layer in conjunction with previous investigations.

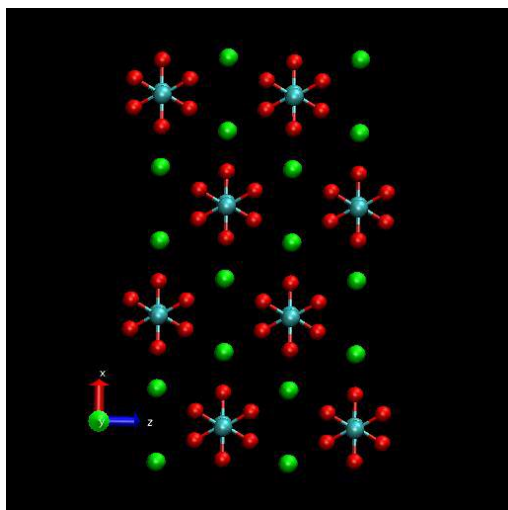


Figure 4. Relaxed BaCO_3 surface in the witerite geometry. One can infer the possibilities for different chemistry to take place as compared to the BaO surface.